Organophosphorus Compounds, XXVI*
The Reaction of Diazoketones with Trialkyl Phosphites

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Diazoketones 1, 8, 10 and 14 react with trialkyl phosphites to give different products depending upon the structure of the diazo compound, the type of the solvent and the nature of the phosphite ester used. Possible reaction mechanisms are discussed and the structural assignments are based on analytical, chemical and spectroscopic results.

Though the action of triphenylphosphine on diazoketones, leading to phosphazines, has been observed frequently1-4, no information in the literature seems to be known regarding the behaviour of these diazo compounds towards trialkyl phosphites.

We have found that when 2-diazo-1,3 indandione (1), was allowed to react with trimethyl-, triethyl-, or triisopropyl phosphite, in benzene or acetonitrile solution, one and the same product was isolated in each case. This was identified as 1,3-indandione-2-hydrazone (4) for the following reasons: I) The yellow crystalline product 4 gave correct combustion values corresponding to the formula C9H6N2O2. II) The IR absorption spectrum of 4, in KBr, lacked the intense band in the 2110-2070 cm⁻¹ region; characteristic for the diazo-group stretching vibration5. However, strong absorption bands at 3300 cm⁻¹ and 3150 cm⁻¹ (NH₂)6 were present in the IR spectrum of 4. III) Treatment of 4 with hydrochloric acid in methanol afforded bis-indandione (6), most probably via an intermediate formation of triketohydridine hydrate (5)7-8. IV) Treatment of compound 4 with mercuric oxide in THF, regenerated the corresponding diazo-compound (1) (m.p., mixed m.p. and comparative IR spectra).

A possible explanation for the production of 1,3-indandione-2-hydrazone (4) is presented in Scheme 1. Initial attack by the phosphite-phosphorus on 1 would give an unstable phosphorazine like 2. Addition of elements of water (unavoidable moisture) to the latter product would give the transient intermediate 3 with pentacovalent phosphorus. This collapses to yield 4. In favour of this idea is the finding that compound 4 and triphenylphosphine oxide are obtained upon treatment of phosphazine (7) with acetic acid in ethanol solution; a behaviour which recalls that of other phosphazines towards hydrolysis9-13.

* Dedicated to Prof. Dr. A. SCHÖNBERG on the occasion of his 85. birthday.

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Similarly, the reaction of 7-diazo-8-acenaphthenone (8) with the same phosphite reagents, gaveacenaphthenequinonemonohydrazone (9) almost quantitatively. The identity of 9 was verified by comparison of its physical properties with a reference sample.

On the other hand, however, the reaction of 3-diazooxindole (10) with trimethyl, triethyl, or triisopropyl phosphite, in benzene or acetonitrile, led to the formation of the azine 13. The latter compound was identical (m.p., mixed m.p. and comparative IR spectra) with an authentic specimen, prepared by hydrolysis of isatine-3-hydrazone. The formation of azine 13 suggested either hydrolysis of an intermediate phosphorazine 11 to the phosphate interaction was conducted in acetonitrile. No reaction was observed with triethyl or trisopropyl in benzene even after 24 h. However, using acetonitrile, as a reaction medium, yielded anthraquinone.

It is evident from the results of the present investigation that diazoketones 1, 8, 10 and 14 behave towards trialkyl phosphites in a manner quite different from PPh₃. In the latter case, stable phosphaazines were isolated. We believe, however, that the reaction of trialkyl phosphites with the diazoketones of the present study involves an initial phosphaazine formation, which suffers further transformation yielding the observed products.

Noteworthy to mention is that the reaction of 2-diazo-1,3-indandione (1) with trialkyl phosphites now represents a newly developed method for preparing 1,3-indandione-2-hydrazone (4), not available by methods known for hydrazone-formation.

**Experimental**

*Materials and equipment*

All melting points are uncorrected. The benzene (thiophene-free) and petroleum ether (b.p. 60–80 °C) were dried over sodium. The trialkyl phosphites were purified by treatment with sodium ribbon followed by fractional distillation. IR spectra were recorded in KBr discs, with a Carl Zeiss Infraord Spectrophotometer Model UR 10. The diazoketones 1, 8, 10 and 14 were prepared by established procedures.

*Action of trialkyl phosphites on 2-diazo-1,3-indandione (1)*

A solution of the trialkyl phosphite (0.012 mole) in benzene (5 ml) was added dropwise to a suspension of 1 (0.01 mole) in benzene and the mixture kept at room temperature for 24 h. After removal of the volatile materials under reduced pressure, the solid product, so obtained, was crystallized from ethanol to give yellow crystals of 1,3-indandione-2-hydrazone (4), melting point 200 °C (75%).
Analysis for C₉H₅N₆O₂
Caled C 61.36 H 3.40 N 16.09,
Found C 61.11 H 3.60 N 16.08.

Compound 4 was also formed when the above described procedure was performed in acetonitrile.

Formation of bis-indandione-1,3-dione (6) from 4
A mixture of 1,3-indandione-2-hydrazone (4) (0.17 g) in aqueous methanol (6 ml 50%) and HCl (0.5 ml sp. gr. 1.18) was refluxed for 3 h. The dark brown precipitate formed, was collected and crystallized from benzene to give 6 (m.p. and mixed m.p. 297 °C)8.

Oxidation of 1,3-indandione-2-hydrazone (4)
A mixture of 4 (0.001 mole) and yellow mercuric oxide (0.0012 mole) in tetrahydrofuran (40 ml) was stirred at room temperature for 24 h. The mixture was then filtered, and the filtrate was evaporated to dryness. The resulting solid material (yield 62%) crystallized from methanol to give yellow crystals identified as 2-diazo-1,3-indandione (1) (m.p., mixed m.p. and comparative IR spectra).

Action of acetic acid on phosphazine 7
A mixture of the phosphazine 7 (0.2 g) and aqueous ethyl alcohol (5 ml 80%) containing one drop of glacial acetic acid was boiled for 1/2 h. The yellow precipitate formed was collected and crystallized from ethanol to give 1,3-indandione-2-hydrazone (4) (m.p. and mixed m.p. 200 °C).

Reaction of trialkyl phosphites with 10-diazoanthrone (14)
A mixture of 10 (0.01 mole), benzene (or acetonitrile) (10 ml) and the trialkyl phosphate (0.012 mole) was kept at room temperature for 24 h. After removal of the volatile materials under reduced pressure, the solid residue, left behind, was crystallized from pyridine to give oxindole-azine 13 (m.p. and mixed m.p. 255 °C) (68%)15.

Reaction of trimethyl phosphite with 10-diazoanthrone (14)
a) In benzene: A mixture of trimethyl phosphate (0.012 mole) and 10-diazoanthrone (0.01 mole)3 in benzene (10 ml) was stirred at room temperature for 72 h. After removal of the volatile materials under reduced pressure, the residue was washed several times with light petroleum. The solid product was then crystallized from toluene to give yellow crystals of anthraquinone (m.p. and mixed m.p. 282 °C) (58%).
b) In acetonitrile: This was carried out in the manner described above. The solid product that was isolated from the reaction mixture was crystallized from pyridine and identified as anthraquinone-azine (16) (m.p. and mixed m.p. 330 °C) (64%)3.

Action of triethyl phosphate on 10-diazoanthrone (14)
a) In benzene: Triethyl phosphate (0.012 mole) was added dropwise to compound 14 (0.01 mole) in benzene (10 ml). The mixture was kept at room temperature for 72 h and the solvent was evaporated in vacuo. The residual solid was washed with light petroleum and crystallized from CCl₄ to give unchanged 14 (m.p. and mixed m.p.) (90%).
b) In acetonitrile: A mixture of 14 (0.01 mole), triethyl phosphate (0.012 mole) and benzene (10 ml) was kept at room temperature for 72 h. After removing the volatile materials under reduced pressure, the solid product left behind, was crystallized from toluene to give anthraquinone (m.p. and mixed m.p. (55%).

Similar results were obtained when the above reaction was repeated using triisopropyl phosphate instead of triethyl phosphate.

7 M. Regitz, Chem. Ber. 97, 2742 [1964].